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Origins and composition of fine atmospheric carbonaceous aerosol in the Sierra Nevada Mountains, California

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Abstract

In this paper we report chemically resolved measurements of organic aerosol (OA) and related tracers during the Biosphere Effects on Aerosols and Photochemistry Experiment (BEARPEX) at the Blodgett Forest Research Station, California. OA contributed the majority of the mass to the fine atmospheric particles and were predominately oxygenated (OOA). The highest concentrations of OA were during sporadic wildfire influence when aged plumes were impacting the site. In situ measurements of particle phase molecular markers were dominated by secondary compounds and could be categorized into three factors or sources: (1) aged biomass burning emissions and oxidized urban emissions, (2) oxidation products of temperature-driven local biogenic emissions and (3) local light-driven emissions and oxidation products. There were multiple biogenic components that contributed to OA at this site whose contributions varied diurnally, seasonally and in response to changing meteorological conditions, e.g., temperature and precipitation events. Concentrations of isoprene oxidation products were larger when temperatures were higher when there were more substantial emissions of isoprene and photochemistry was enhanced. While methyl chavicol oxidation contributed similarly to OA during both identified meteorological periods. In contrast, the abundances of monoterpene oxidation products were greater during cooler conditions, even though emissions of the precursors were lower. Following the first precipitation event of the fall the abundances increased dramatically, although the mechanism responsible is not known. OA was correlated with alkyl nitrates and carbon monoxide (CO), consistent with previous observations, while being comprised of mostly non-fossil carbon (> 75 %). The correlation between OA and an anthropogenic tracer does not necessarily identify the source of the carbon as being anthropogenic but instead suggests a coupling between the anthropogenic and biogenic components in the air mass that might be related to the source of the oxidant and/or the aerosol sulfate. Observations of organosulfates of isoprene and α -pinene provided evidence for the likely importance of aerosol sulfate in spite of neutralized aerosol. This is in contrast to laboratory studies where strongly acidic seed aerosols were needed in order to form these compounds. These compounds together represented only a minor fraction (< 1 %) of the total OA mass and suggest that other mechanisms, e.g., NO_x enhancement of oxidant levels, are more likely to be responsible for the majority of the anthropogenic enhancement of biogenic secondary organic aerosol observed at this site.

1. Introduction

Fine atmospheric particulate matter, defined as having aerodynamic diameters less than 2.5 μm ($\text{PM}_{2.5}$), affects visibility, human health and the Earth's climate. Organic aerosols (OA) constitute an important fraction (20 – 90 %) of the fine particle mass [Kanakidou *et al.*, 2005] and are ubiquitous throughout the northern hemisphere [Zhang *et al.*, 2007a]. OA originates from both anthropogenic and biogenic sources and can be emitted directly to the atmosphere as primary organic aerosol (POA) or formed through gas to particle conversion of low-volatility compounds as secondary organic aerosol (SOA) [Seinfeld and Pankow, 2003]. SOA accounts for the majority of the total organic mass of aerosols [Zhang *et al.*, 2005; 2007a] and traditional models likely underestimate SOA by factors of 2 – 10 in polluted regions [de Gouw *et al.*, 2005; Heald *et al.*, 2005; Volkamer *et al.*, 2006; Heald *et al.*, 2010; Spracklen *et al.*, 2011], but not in 'clean' biogenic regions [e.g., Tunved *et al.*, 2006; Chen *et al.*, 2009; Hodzic *et al.*, 2010b; Slowik *et al.*, 2010]. More recent models achieve closure and even over-predict SOA formation in polluted regions, but a low level of confidence remains in the identification of the important precursors and pathways for the observed SOA [Dzepina *et al.*, 2009; Hodzic *et al.*, 2010a; Tsimpidi *et al.*, 2010]. Possible hypothesis for the observed OA discrepancies between measurements and models are: (1) as yet unidentified precursor species not included in traditional models [Goldstein and Galbally, 2007; Robinson *et al.*, 2007; de Gouw *et al.*, 2011], (2) higher yields of known precursors than included in traditional models [Tsimpidi *et al.*, 2010], (3) aqueous chemistry in clouds and aerosols, [Ervens *et al.*, 2008] and (4) heterogeneous uptake of gas phase species, e.g., glyoxal [Kroll *et al.*, 2005; Volkamer *et al.*, 2007].

Since estimated emissions of biogenic volatile organic compounds (BVOCs) exceed those of anthropogenic VOC emissions by over an order of magnitude [Guenther *et al.*, 1995; Middleton, 1995] global models have traditionally attributed a large fraction of SOA to biogenic sources [Kanakidou *et al.*, 2005]. However, recent global modeling studies suggest a substantial global role for anthropogenic or anthropogenically-influenced SOA formation [Pye and Seinfeld, 2010; Spracklen *et al.*, 2011]. The contributions of anthropogenic and biogenic sources to OA have previously been estimated using several indirect approaches, e.g., chemical mass balance (CMB) [Schauer *et al.*, 1996; Kleindienst *et al.*, 2010], organic tracer based method [Offenberg *et al.*, 2011] and measurements of the radiogenic carbon (^{14}C) content [Szidat *et al.*, 2004]. The determination of the ^{14}C content provides mass weighted source apportionment of carbonaceous aerosol particles due to the direct distinction between non-fossil and fossil carbon. Radiogenic carbon (^{14}C) is present in a small but approximately constant level in contemporary or living materials but is absent in fossil fuels as a result of radioactive decay. Moreover, ^{14}C is a robust 'tracer' as it retains its identity throughout any chemical transformation. Recently, this approach has been used to show that a large fraction of carbonaceous aerosol in the United States is non-fossil in origin; ~50 % in urban areas and 70 – 100 % in near urban and remote sites [e.g., Bench *et al.*, 2007; Schichtel *et al.*, 2008]. Not all this non-fossil carbon in aerosols can be attributed to SOA formed from BVOC oxidation because there are important non-negligible contributions from biomass burning, biofuel use and other non-fossil urban OA sources [Hildemann *et al.*, 1994; Hodzic *et al.*, 2010b]. It is possible that 30 – 50 % of the non-fossil carbon is attributable

to urban sources, as suggested by Hodzic et al. [2010b] for Mexico City though this is not known for Northern California, which has implications for the interpretation of the magnitude of the non-fossil fraction.

In previous studies, OA has been observed to be correlated with tracers of anthropogenic influence, e.g., CO [Sullivan et al., 2006; Weber et al., 2007; Bahreini et al., 2009] and alkyl nitrates [de Gouw et al., 2005]. Similar proportions of OA to 2-propyl nitrate were observed in the northeastern United States and northern Georgia despite major differences (10 – 100 times) in BVOC concentrations. ¹⁴C measurements associated with the northern Georgia dataset indicate that the water soluble organic carbon (WSOC) was predominantly (> 70 %) non-fossil and a substantial fraction was likely formed through secondary processes involving BVOC and an anthropogenic component that may be the controlling factor [Weber et al., 2007]. It has been suggested that biogenic SOA formation may be enhanced in polluted air [Weber et al., 2007; Goldstein et al., 2009; Hoyle et al., 2011; Spracklen et al., 2011] and several recent studies have suggested a possible coupling between anthropogenically emitted species and BVOCs in SOA formation, e.g., (i) the nocturnal oxidation of isoprene by NO₃ contributed, on average, ~6 % to SOA in the northeastern United States and exceeded SOA derived from OH photooxidation of isoprene by ~50 % [Brown et al., 2009], (ii) Chan et al., [2010] showed that the aerosol yield from isoprene photooxidation was strongly dependent on the NO₂:NO ratio under high NO_x conditions and also reported the highest aerosol yields (~ 7 %) for isoprene oxidation with NO₂:NO ratios of > 5:1, and (iii) Surratt et al., [2006; 2007] have shown the presence of particle phase organosulfate and nitroxyorganosulfate compounds derived from the oxidation of BVOCs, which have been estimated to contribute ~10 % to the total organic aerosol mass in some locations [Surratt et al., 2008].

The formation of organosulfates has been speculated to be a major contributor to the observed enhancements in laboratory SOA yields in the presence of acidic aerosols [Surratt et al., 2007; 2010; Chan et al., 2011]. Previous chamber studies of anthropogenic precursor oxidation have not shown as strong a dependence of SOA mass on the presence of aerosol acidity as for BVOCs. This suggests that uptake of BVOC oxidation products to produce organosulfates could be a mechanism that selectively incorporates non-fossil carbon into the condensed phase while maintaining a dependence of OA on anthropogenic emissions, i.e., sulfur dioxide (SO₂). As SO₂ emissions are strongly related to combustion, a substantial source of both carbon monoxide (CO) and NO_x, this would be consistent with the observations of correlations between OA and both CO and alkyl nitrates, although in some locations where CO and SO_x were not correlated, SOA was still correlated with CO [DeCarlo et al., 2010]. However, previous field measurements have not observed evidence of acid catalyzed SOA formation, e.g., in power plant plumes over Atlanta, Georgia [Peltier et al., 2007] or in Pittsburgh, Pennsylvania [Takahama et al., 2006; Zhang et al., 2007b]. This suggests there may be important differences between organosulfate formation observed in the laboratory relative to the atmosphere, which has implications for the interpretation of ambient data using models informed from smog chamber experiments.

The implications of the couplings between anthropogenic and biogenic compounds in SOA formation are that the presence of substantial biogenic carbon does not necessarily mean that aerosols are natural, i.e., uncontrolled by anthropogenic emissions. Indeed, a recent regional modeling study has illustrated the potential influence of anthropogenic emissions, in particular primary organic particulate matter and nitrogen oxides (NO_x) on increasing biogenic SOA formation by a factor of 2 [Carlton *et al.*, 2010]. They showed that in their model higher NO_x concentrations generated more ozone that led to increased hydroxyl radical (OH) concentrations and enhanced oxidation of BVOCs and POA and SOA from anthropogenic and biomass burning emissions lead to enhanced partitioning of BSOA. A global modeling study has suggested an even larger enhancement approaching an order of magnitude, whose mechanistic causes are not understood [Spracklen *et al.*, 2011].

In this paper, we report measurements made at the Blodgett Forest Research Station during the Biosphere Effects on Aerosols and Photochemistry Experiment (BEARPEX). The site is located between the city of Sacramento and Lake Tahoe and is impacted by both urban emissions and substantial biogenic sources that are located both upwind of and at the site. Previous work at this site has shown that: (i) chemical loss of ozone was likely due to gas-phase reactions with BVOCs emitted from the forest in a similar temperature dependent manner to terpenes [Kurpius and Goldstein, 2003], (ii) there is a substantial flux of reactive monoterpenes, sesquiterpenes and methyl chavicol from the forest to the atmosphere [Holzinger *et al.*, 2005; Bouvier-Brown *et al.*, 2009a; 2009b], and (iii) the presence of large quantities of BVOC oxidation products above the canopy indicates substantial oxidation of BVOCs within the forest canopy [Holzinger *et al.*, 2005]. Lunden *et al.* [2006] observed fine aerosol growth events at the Blodgett Forest site, which are understood to be related to terpene oxidation within the forest canopy. Previous filter measurements at the site [Cahill *et al.*, 2006] have shown the presence of several known biogenic oxidation products in the particle phase whose concentrations were substantially elevated at night. This site provides an opportunity to examine aerosol formation in a low NO_x, high VOC regime with substantial contributions from biogenic sources. In this work, we use chemically resolved measurements of organic aerosol and related tracers to characterize the chemical composition of carbonaceous aerosols, determine their sources at Blodgett Forest and investigate the coupling between anthropogenic and biogenic emissions in the formation of SOA in this environment.

2. Experimental Methodology

2.1 Site description

The BEARPEX campaign took place at a ponderosa pine (*Pinus ponderosa* L.) plantation owned by Sierra Pacific Industries adjacent to the University of California – Blodgett Forest Research Station (UC-BFRS; 38.90°N, 120.63°W, 1315m elevation above sea level). The site is located between Sacramento and Lake Tahoe in the Sierra Nevada Mountains, California, and was established as an atmospheric measurement site in 1997 [Goldstein *et al.*, 2000]. The site was planted with ponderosa pine in 1990, which in 2007 had a mean height of 8 meters. The understory is composed primarily of Manzanita (*Arctostaphylos* spp.) and whitethorn (*Ceanothus cordulatus*) shrubs. The campaign ran from 15th August to October 10th 2007 and captured two distinct meteorological periods,

the first from August 15th – September 12th period was characterized by hot and dry conditions and sporadic influence of smoke from various California wildfires. A sharp decline in temperature and a simultaneous increase in relative humidity occurred between September 12th and 13th, which led to cooler and wetter conditions that persisted for the remainder of the campaign. This later period also experienced several precipitation events on September 20th, 22nd, 23rd and snow on October 5th.

2.2 In-situ measurements

A wide range of instrumentation measuring concentrations, gradients and fluxes of a broad suite of gas- and particle-phase constituents were deployed during the BEARPEX campaign providing a very comprehensive dataset. Measurements included ozone, nitrogen oxides, nitric and nitrous acid, organic nitrates, organic peroxides, formaldehyde, glyoxal, volatile organic compounds, chemically resolved aerosol speciation and speciated organic aerosol composition. In this section we describe only the measurements discussed in this paper.

Measurements of non-refractory PM₁ aerosol components were made using a high-resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS; Aerodyne Research Inc.) for 42 days from 19th August – 29th September 2007. The operation of the AMS has been described in detail elsewhere [Jayne *et al.*, 2000; Jimenez *et al.*, 2003; DeCarlo *et al.*, 2006] and details specific to BEARPEX were described by Farmer *et al.* [2011]. In brief, aerosol particles were continuously drawn through a dedicated 1/2" insulated copper inlet from the top of the north tower and were focused through an aerodynamic lens and impacted onto a vaporizer held at ~600 °C. The vapors were ionized with electron ionization and the resultant ions were detected byToFMS. Chemically resolved mass concentrations of individual components (organics, sulfate, nitrate, ammonium and chloride) were extracted from the AMS raw data following the work of Allan *et al.* [2004] and DeCarlo *et al.* [2006]. The organic fraction was further separated into 'oxygenated-like' (OOA) and 'hydrocarbon-like' (HOA) organic aerosols using a positive matrix factorization approach, previously described by Docherty *et al.* [2008].

A wide range of volatile organic compounds (VOC) and oxygenated volatile organic carbon (OVOC) compounds were measured by two independent in situ GC/MS instruments operated by the University of California, Berkeley [Bouvier-Brown *et al.*, 2009a; 2009b] and by the National Oceanic and Atmospheric Administration (NOAA) [Goldan *et al.*, 2004] for 51 and 39 days from 20th August – 10th October 2007 and 21st August – 28th September, respectively. Detailed descriptions of both these instruments have previously been published for this campaign by [Bouvier-Brown *et al.*, 2009a; 2009b]. The influence of emissions from the propane generator, which was used to power the site and whose emissions were frequently observed at the site during low windspeeds, has been removed by filtering the data for acetylene to benzene ratios greater than 10:1.

Speciated measurements of molecular marker compounds in aerosols were made by thermal desorption aerosol gas chromatography (TAG) coupled with mass spectrometry for 31 days from 7th September – 8th October 2007. This instrument has been described

in detail by Williams et al. [2006] and further developments to the TAG system have been discussed in Williams et al. [2007] and Kreisberg et al. [2009]. Thus, only a brief description is given here. Aerosol samples (PM_{2.5}) were drawn at a sampling rate of 9 L min⁻¹ for 90 minutes (sample volume 0.75 m³) from a dedicated insulated stainless steel inlet line from a height of approximately 9.2 m. Aerosols were humidified and impacted in a custom collection and thermal desorption cell (CTD) at ambient temperature. Following sample collection, the CTD was then heated to 300°C to transfer and refocus all the analytes onto the head of the chromatographic column; analytes were detected by electron ionization quadrupole mass spectrometry operated in full scan mode with *m/z* range of 29 – 400. The introduction of calibration standards was done manually, as described by Kreisberg et al. [2009]. Several instrumental improvements, not described in previous publications, were made prior to the BEARPEX campaign. Firstly, all temperature controls, valve switching and data logging were controlled using in-house written software (Labview, National Instruments). Secondly, the thermal control system of two critical sample transfer lines was redesigned. This involved encapsulating each transfer tube in an aluminum block to increase the thermal mass facilitating higher (300°C) and more consistent temperature control. The improved transfer efficiency achieved by these refinements was tested using an n-alkane injection standard. The improved system detects compounds with vapor pressures up to the equivalent of tetracontane (C₄₀ alkane; subcooled liquid vapor pressure = 2.73x10⁻⁷ Pa at 298K, saturation concentration *c** = 0.06 µg m⁻³) that were not observed with the unmodified instrument [Kreisberg et al., 2009]. Finally, active heating control of the humidifier was introduced to ensure bounce-free particle collection through maintaining a relative humidity of >75 % in the collection and thermal desorption cell during sampling. To avoid condensing any water between the humidifier and the cell, an additional heating element and PID controller were used to maintain the connecting plumbing between the cell and humidifier approximately 2 °C above the cell temperature. With this setup it was possible to maintain the cell relative humidity between 75% and 85% under nearly all ambient sampling conditions encountered and thus provide bounce-free collection of 0.08 – 2.5 µm particles.

2.3 Offline filter measurements

The speciated molecular markers that are measurable by TAG span a wide range of organic compounds [Williams et al., 2006; 2007; 2010b] but TAG performs best for species that are in the low to intermediate polarity range (e.g., n-alkanes to > C₁₀ monocarboxylic acids) and typically with carbon to oxygen (O/C) ratios of 0.3 or less, though some compounds have been observed by TAG that have an O/C of up to 0.6 [Williams et al., 2010a], comparable to the SV-OOA (previously OOA-2) factor frequently described from AMS measurements [Aiken et al., 2008; Jimenez et al., 2009]. Highly oxidized and thermally labile components do not pass through the chromatography column or are decomposed during thermal desorption and thus either do not reach the detector or are not detected in their original form. Lower time resolution filter measurements of these types of compounds can be a useful complement to the high time resolution TAG measurements for obtaining a more complete picture of organic aerosol composition.

High-volume filter samples (26 in total) were collected adjacent to the TAG inlet at 9.3 m from September 20th – October 1st 2007. The samples were collected using a Thermo Anderson Total Suspended Particulate (TSP) high volume (Hi-Vol) sampler with an SA-230-F impaction plate at a volumetric flow of 68 m³/hour, as previously described by Bench and Herckes [2004]. The impaction plate removes particles with diameters larger than 2.5 µm. Samples were collected for between 6 and 12 hours on a 20 cm x 25 cm quartz fiber filter (Gelman QM-A). The quartz filters were pre-fired by baking at 600 °C for 12 hours and stored in sealed plastic bags prior to use. After sampling the quartz filters were immediately placed in pre-baked aluminum foil and stored frozen until analyzed. A field blank was obtained by placing one filter in the sampler for ten minutes with the pump off on September 26th, the midpoint of the sampling period. These filters were collected during only the cold period of the campaign and are not representative of the entire campaign. Therefore, additional high-volume filter samples (17 in total including a field blank) were collected following the identical sampling protocol at the same height and on the same tower from July 26th – July 31st 2009 during a follow up campaign. These filters were collected when meteorological conditions were similar to the earlier part of the 2007 campaign, although there was no incidence of wildfire influence during the 2009 sampling period.

2.3.1 Radiogenic carbon (¹⁴C) analysis

Eight of the 2007 filters, selected for their higher organic aerosol loadings, based on concurrent AMS measurements, were analyzed for their radiogenic carbon (¹⁴C) content by accelerator mass spectrometry at the Lawrence Livermore National Laboratory (LLNL), as previously described by Bench and Kerckes [2004]. Briefly, 36 cm² (6 x 6 cm) samples were cut from the central region of each quartz filter, sealed under vacuum with copper oxide oxidizer in a quartz tube and combusted at 900 °C. Carbon dioxide from the combustion was cryogenically isolated from other combustion products and measured manometrically before conversion to graphite by hydrogen reduction using an iron catalyst. The ¹⁴C/C ratios in the graphite samples were measured by accelerator mass spectrometry. The data are reported as a fraction of the modern radiocarbon standard [Stuiver and Polach, 1977] and have been corrected for the nuclear bomb pulse effect by dividing the fraction of modern carbon by 1.06, to account for the additional modern carbon content in the current atmosphere [Levin *et al.*, 2010]. No correction for the contribution of biomass burning to non-fossil carbon [Aiken *et al.*, 2010] was made because the filters were all collected during a period with no substantial biomass burning influence. The ¹⁴C measurements were also corrected for isotopic fractionation effects using a $\delta^{13}\text{C}$ value of –25 per mil [Stuiver and Polach, 1977], though the magnitude of this correction was small and had a minimal effect on the radiocarbon values.

2.3.2 Organosulfate and nitrooxy-organosulfate analysis

Aliquots (100 cm²) of 15 of the filters collected between September 20th and September 25th 2007 and all 16 of the filters collected in 2009 were analyzed for organosulfates and nitrooxyorganosulfates. These filters represented two continuous five day periods, one in each year, with three filters per day that provided an uninterrupted time series with sufficient time resolution to separate the influence of local early morning biogenic emissions from the afternoon arrival of the urban plume from Sacramento and nighttime

chemistry. Samples were analyzed by ultra performance liquid chromatography coupled to electrospray ionization high-resolution time-of-flight mass spectrometry (UPLC/ESI-HR-TOFMS) at the California Institute of Technology (Caltech). Identically sized aliquots of the same filters were also analyzed by high performance liquid chromatography coupled to electrospray ionization high-resolution quadrupole time-of-flight mass spectrometry (HPLC/ESI-HR-QTOFMS) at the University of Aarhus, Denmark. The analytical methodologies have previously been described by Surratt et al. [2008] (Caltech) and Kristensen and Glasius [2011] (Aarhus). Briefly, organosulfates and nitrooxyorganosulfates were detected as deprotonated ions in the negative ion mode at both institutions using reverse-phase chromatography. At Caltech concentrations were assigned from relative responses to authentic organosulfate standards derived from the epoxide of butadiene (BEPOX) and β -pinene oxide for all isoprene and monoterpene derived organosulfates, respectively. At Aarhus, camphor sulfonic acid was used as a surrogate standard for all the organosulfates.

3. Results and discussion

3.1 Bulk aerosol measurements

Figure 1a shows a stacked time series plot of aerosol components (organics, sulfate, nitrate, ammonium and chloride) as measured by the AMS. Organics were the dominant fraction ($\sim 75\%$) contributing on average $3\ \mu\text{g m}^{-3}$ to the total aerosol mass. Of the inorganic components, sulfate was the most abundant contributing on average $0.6\ \mu\text{g m}^{-3}$ to the total ($\sim 15\%$). Ammonium and nitrate contributed on average $0.3\ \mu\text{g m}^{-3}$ ($\sim 7\%$) and $0.2\ \mu\text{g m}^{-3}$ ($\sim 5\%$), respectively, and the aerosol was approximately neutralized without excess H^+ [Farmer et al., 2011]. Substantial varieties and concentrations of organosulfates and nitrooxyorganosulfates were observed at this site (see section 3.7) and are detected by the AMS [Farmer et al., 2010]. As such the observed nitrate and sulfate concentrations reported here represent the combined total of both inorganic and organic species. Figure 1b shows a time series plot of the AMS factors, ‘oxygenated-like’ organic aerosol (OOA) and ‘hydrocarbon-like’ organic aerosol (HOA), along with acetonitrile, a known gas phase tracer for biomass burning [de Gouw and Warneke, 2007]. The OOA fraction was dominant throughout the campaign and the highest concentrations were associated with biomass burning influence at the site, as indicated by elevated acetonitrile concentrations. Grieshop et al. [2009] and Cubison et al. [2011] have recently summarized the aging of biomass burning emissions to form OOA in laboratory and field studies, respectively. Thus the increased OOA is consistent with the impact of aged biomass burning plumes. A scatter plot of OOA versus acetonitrile (Figure S1a; supplementary information) shows a strong positive correlation ($R^2 = 0.67$, $n = 273$) during periods of biomass burning influence (acetonitrile > 0.175 ppb) [de Gouw and Warneke, 2007]. However, during all other periods (acetonitrile < 0.175 ppb) this relationship was very poor ($R^2 = 0.21$, $n = 1398$) indicating that biomass burning was not an important source of OOA outside of the sporadic wildfire plumes.

3.2 Carbonaceous Aerosol: Non-fossil or Fossil

Table 1 summarizes the data from the radiogenic carbon (^{14}C) analysis along with the organic carbon measured by the AMS averaged over the same time periods as the filters. The AMS data has been converted from $\mu\text{g m}^{-3}$ to $\mu\text{g C m}^{-3}$ assuming a organic matter to

organic carbon (OM/OC) ratio of 1.9 for OOA aerosol [Aiken *et al.*, 2008]. The total carbon mass loading on the 36 cm² filter punches ranged from 300 – 560 µg C, which were in some cases close to the 210 µg C mass on the field blank and thus involved a non-negligible blank correction. As such, analytical uncertainties were generally higher than previous publications of ¹⁴C analyses. A plot of the measured sample volume to detected carbon mass collected yielded a good positive correlation ($r = 0.88$, $n = 8$) giving confidence in the filter collection and analytical methodology. A plot of the organic carbon measured on the filters versus the AMS is shown in Figure S2 (supplementary information). There is very little variability in both these measures of OC, which explains the lack of a stronger correlation. More importantly, the OC measured on the filter is about three times larger than the OC measured by the AMS. Therefore, it is likely that there was gas phase adsorption into the filter during sample collection since no denuder could be used at the high flow rates necessary for the ¹⁴C measurements and that at these very low OC concentrations the presence of gas phase biogenic compounds could bias the observed ¹⁴C measurements. On average, the non-fossil fraction was determined to be 0.84 ± 0.19 (mean \pm standard deviation) of the total measured aerosol carbon. This indicates the likely importance of non-fossil (a major fraction of which is presumably biogenic) carbon to the total carbonaceous aerosol at the Blodgett site. It is likely that this also includes non-negligible contributions from urban sources, which can roughly be estimated as follows: the fossil fraction is 0.16 and by assuming urban emissions are 30 % then $(0.3/0.7) \times 0.16 = 0.07$. Therefore, if 0.07 of the 0.84 is from pollution sources then 0.77 remains that is presumably from biogenic sources.

3.3 Relationship between organic aerosol and anthropogenic tracers

A strong positive relationship was observed between OA and 2-propyl nitrate (Figure 2a), similar to previous studies [de Gouw *et al.*, 2005; Weber *et al.*, 2007]. The BEARPEX data in this figure have been color coded by acetonitrile and in the absence of biomass burning influence (i.e., acetonitrile < 0.175 ppbv) there is very good agreement between the BEARPEX and New England Air Quality Study (NEAQS) data [de Gouw *et al.*, 2005]. The meteorological dynamics at the Blodgett site may introduce misleading correlations owing to its topographical location in the foothills of the Sierra Nevada Mountains. It may be possible to filter out this interference by looking at the same correlation for specific times of day, e.g., early morning (07:00 – 09:00), midday (12:00 – 14:00) and early evening (19:00 – 21:00). Figure 2b shows that the correlation for these three selected time periods are all strong positive relationships with identical slopes, within the uncertainties of the fits, as the entire dataset giving us confidence that this relationship results from chemistry and is not caused by similar transport pathways. The slope between OA and 2-propyl nitrate correlations was 20 % lower during BEARPEX compared to NEAQS [de Gouw *et al.*, 2005] indicating that SOA production may have been slightly less efficient in the 2007 Sacramento plume relative to 2002 New York plume.

OA was also correlated to CO (slope = 0.04 ± 0.002 µg sm⁻³ OA per ppb CO, $R^2 = 0.79$, $n = 576$; Figure S2 supplementary information), which is again consistent with previous measurements [Sullivan *et al.*, 2006; Weber *et al.*, 2007; Bahreini *et al.*, 2009].

The CO data has been filtered for acetonitrile > 0.175 ppb to remove influence from biomass burning, as this is known to be a significant source of CO [Andreae and Merlet, 2001]. The CO data in this figure have also been filtered by wind speeds < 1 m/s to remove the sporadic influence of the onsite generator. CO is a combustion tracer, so in the absence of biomass burning, a correlation to OA indicates a relationship between anthropogenic derived emissions from combustion sources to OA. However, CO can also be produced from the oxidation of anthropogenic and biogenic hydrocarbons. Chemical production of CO from the oxidation of anthropogenic VOCs is thought to be negligible within these timescales [Griffin *et al.*, 2007]. Conversely, chemical production of CO from biogenic VOCs is likely non-negligible, e.g., Hudman *et al.* [2008] reported that the source of CO in the Southeast US during summer was dominated by BVOC oxidation although this analysis has not been done for our site. Slowik *et al.* [2010] estimated in Eastern Canada that a large contribution of biogenic CO (~ 100 ppbv for ~ 15 $\mu\text{g m}^{-3}$ of OA) derived from terpene oxidation. During the hot period we observe ~ 2.5 $\mu\text{g m}^{-3}$ of OA, which is thought to be biogenic. So if we scale our observations to Slowik *et al.* [2010] we estimate that 16 ppb of CO, or one sixth of the excess CO they observed during their identified 'biogenic event', was from BVOC oxidation at Blodgett Forest. This is small relative to the observed enhancement but is not a negligible contribution. In contrast to Eastern Canada, Blodgett forest is dominated by isoprene emissions, which are partially oxidized on arrival at the site. Isoprene SOA yields for OH photooxidation are reportedly lower than for the terpenes (< 7 % versus 3 – 27 %) [Griffin *et al.*, 1999; Chan *et al.*, 2010] while the CO yields are reportedly similar, ~0.2 molecules of CO per carbon atom [Duncan *et al.*, 2007]. This implies that this estimate is very likely an upper limit and as such that the majority of the CO observed at the site is not biogenic in origin. The correlation between CO and OA at Blodgett Forest indicates a possible coupling between OA and something emitted concurrently to combustion derived CO, e.g., NO_x and/or SO₂.

3.4 Diurnal variations in organic aerosol and gas phase tracers

As a result of strong orographic forcing, the daily pattern of winds impacting the Blodgett Forest site are nearly constant in speed and direction [Murphy *et al.*, 2006; Day *et al.*, 2009], and as a result, averaged daily profiles are highly representative of diurnal behavior at this site. Figure 3 shows the average diurnal profiles for organic aerosol (OA), isopentane, α -pinene and the sum of methyl vinyl ketone (MVK) and methacrolein (MACR) for the two different meteorological periods (hot and cold) as defined in section 2.1.

Isopentane is a tracer for urban influence as it is known to be emitted from both vehicle exhaust and evaporation of gasoline fuel [Gentner *et al.*, 2009]. Mixing ratios of isopentane ranged from 30 – 90 pptv and 30 – 50 pptv in the hot and cold periods, respectively. Mixing ratios generally increased throughout the day during both meteorological periods, illustrating the transport of urban pollution from Sacramento and the Central Valley, which maximizes late in the day. Differences between the hot and cold periods likely reflect differences in the contributions of evaporative emissions from gasoline and/or changes in the efficiency of transport from the Central Valley to Blodgett Forest. MVK and MACR are the major first generation products from the atmospheric

oxidation of isoprene [Pierotti *et al.*, 1990]. Mixing ratios of MVK + MACR are lowest in the morning and increase sharply with a maximum just after noon, reflecting the transport and oxidation of isoprene emissions from a band of Oak trees several hours upwind of the Blodgett site [Dreyfus *et al.*, 2002]. Identical diurnal variations are observed during both periods, although observed mixing ratios are a factor of ~6 lower during the cold period as a result of reduced isoprene concentrations caused by the strong temperature and light dependence of its emission [Guenther *et al.*, 1993]. α -pinene is a monoterpene known to be emitted locally from the ponderosa pine trees present at the site [Schade *et al.*, 1999; Bouvier-Brown *et al.*, 2007; 2009a] and shows two maxima. The first maximum is early in the morning and is the result of light-driven emissions accumulating in the shallow boundary layer. The second maximum in α -pinene is in the late evening when temperature-driven emissions accumulate in the shallow nocturnal boundary layer. Other locally emitted biogenic compounds, e.g., 2-methyl-3-buten-2-ol (MBO) [Schade and Goldstein, 2001] and methyl chavicol [Bouvier-Brown *et al.*, 2009b], also exhibit this behavior. These features are observed in both meteorological periods although the magnitude for α -pinene is, on average, a factor of ~3 lower during the cold period while methyl chavicol was about the same during both periods (Figure 5). Monoterpene emissions have been reported to be dependent on relative humidity [Schade *et al.*, 1999] and concentrations of several monoterpenes were observed to increase, relative to the cold period, following the first rain events on September 20th [Bouvier-Brown *et al.*, 2009a]. However, these concentrations were still lower than those during the hot period. Methyl chavicol concentrations were also reported to respond to rain although there was a delay of several days relative to the monoterpenes [Bouvier-Brown *et al.*, 2009b].

In contrast to the gas-phase tracers shown in Figure 3, the diurnally averaged OA concentrations changed by less than a factor of 2 throughout the day during both the hot and cold periods, which may temper the statement that most of the OA is derived from biogenic sources. However, as we will show in this paper there are multiple components to BSOA whose contributions change not only diurnally but also seasonally. Additionally, the fraction of oxidation products that become incorporated into the aerosol phase may be dependent on more factors than simply the emission rate of the precursors. Figure 4 shows how the MVK+MACR concentrations, a proxy for isoprene oxidation products, decline from the hot to the cold periods and that their abundances are not affected by the onset of rain in mid-September. As will be shown in section 3.7 this is generally consistent with the behavior of the isoprene derived organosulfates whose concentrations were higher during hotter conditions. Figure 4 also shows how the abundance of two particle-phase tracers of terpene oxidation, pinonaldehyde and nopinone derived from α -pinene and β -pinene, respectively (these compounds are likely present as particle phase oligomers, see section 3.6), increase by more than a factor of 5 following the first rain event and remain elevated for more than a week. As a result the observed OA is a superposition of contributions that maximize during both day and night and are influenced by not only the emission rate of the precursor compounds, but also by additional factors that control the uptake of the oxidation products into the aerosol phase. Isoprene oxidation products appear to be a dominant component of BSOA during the hot period when emissions of isoprene are the largest, while during the cold period terpene

oxidation products are a more substantial contributor to BSOA. Other particle-phase molecular markers also show large changes in their abundances by factors of 2 – 20 (Figure 4) indicating that sources of OA were changing both throughout the day and as the season progressed from summer into fall.

3.5 In situ particle phase molecular markers

The gas chromatograms obtained by the TAG instrument were dominated by early eluting predominately secondary organic compounds (or their decomposition products, see below) consistent with the predominance of the oxygenated organic aerosol (OOA) fraction (~85 %) as determined from AMS measurements. In total, 65 individual compounds were detected and continuously tracked by TAG. Species identification was either by retention time matching to known standards or from mass spectral matching to a commercially available library of mass spectra (NIST 2008); more than 80 % of the detected peaks were identified. Relative abundance timelines were constructed for all these compounds after correcting for abundances in the filtered ambient samples (i.e., particle phase = ambient – filtered ambient).

Similar to previous work [Williams *et al.*, 2007; 2010b], compounds that did not match specific criteria were removed prior to performing a factor analysis. In this work the criteria applied were that compounds must be less than 30 % in the gas phase to avoid large subtractions and each compound's particle-phase timeline must have a coefficient of determination (R) > 0.7 with its ambient (gas + particle) timeline indicating that most of the variability was conserved after subtracting the gas-phase portion. Also, compounds that were below the detection limits for more than 30 % of the study have been removed to maximize the number of data points, leaving a total of 21 individual compounds. A complete list of these compounds including molecular formulas and an estimate of uncertainty in compound identification are given in Table 2. Factor analysis was performed in SPLUS 6.2 (MathSoft, Inc.), using varimax rotation and principal factors extraction, similar to previous work [Williams *et al.*, 2007]. The input parameters fit best to 3 different factors that can be thought of as signatures of specific sources or transformation processes (Table 2). Additional factors individually explained less than 2% of the variance, or less than half of the smallest contributing factor, and therefore were not included in the analysis.

Figure 5 shows the temporal and diurnal trends of four major tracers (phthalic acid, levoglucosenone, pinonaldehyde and methyl chavicol), during both meteorological periods. These represent the three major factors or sources identified from the factor analysis (Table 2). Phthalic acid and levoglucosenone load into the same factor and will be discussed in more detail below. We observe fewer factors than a similar analysis for gas-phase species by Lamanna and Goldstein [1999] who reported six factors for the same site. However, the general source categories; anthropogenic and biomass burning emissions, temperature-dependent biogenic emissions and temperature-and light-driven biogenic emissions, are consistent between the two analyses. It is important to note that isoprene oxidation products, e.g., the methyl tetrols, have previously been observed in the particle phase at the site [Cahill *et al.*, 2006], although as a result of their high polarity are not observable with TAG. As a result there were no good tracers of isoprene SOA in the TAG dataset, which clearly impacts any source apportionment approach because

isoprene and its oxidation products are likely an important source at the site. Several organosulfate and nitrooxy-organosulfate products of isoprene oxidation were detected following the analysis of high-volume filter samples and will be discussed further in section 3.7.

Factor 1: Aged biomass burning and oxidized urban emissions

The first factor accounted for ~38 % of the variance and included a mixture of compounds that likely represent aged biomass burning emissions and oxidized urban emissions. Compounds loading onto this factor included phthalic acid and 3-methyl and 4-methyl phthalic acids, benzoic acid, levoglucosenone and three aromatic ketones (1H-isoindole-1,3-(2H)-dione, 1H-indene-1,3-(2H)-dione and 1-(3H)-isobenzofuranone). All compounds loading onto this factor were well correlated with acetonitrile ($R^2 > 0.64$, $n = 87$), which is partially due to the high dynamic range of both tracers due to the biomass burning plumes around September 7th – 9th. This indicates the importance of biomass burning to this factor at the end of the hot period. It seems likely that levoglucosenone is an oxidation product of levoglucosan, a known biomass burning marker [Simoneit *et al.*, 1999], and may indicate the aged influence of this source. Ma and Hays [2008] reported the observation of 1H-isoindole-1,3-(2H)-dione in aerosols emitted from agricultural fires. There are no clear diurnal variations in either of these markers consistent with the sporadic nature of biomass burning influence. However, the highest concentrations were observed in the afternoon, indicating the importance of upslope flow conditions for bringing aged fire plumes to Blodgett Forest during these events.

Phthalic acid is formed from the rapid particle-phase hydrolysis of phthalic anhydride that is a major product from the photooxidation of naphthalene under both high- and low- NO_x conditions [Wang *et al.*, 2007; Kautzman *et al.*, 2010]. Naphthalene is emitted directly from diesel exhaust [Rhead and Pemberton, 1996] and biomass burning [Jenkins *et al.*, 1996]. Phthalic acid is reportedly found in high concentrations in the atmosphere and has been suggested as a single-species surrogate for the contribution of anthropogenic SOA to ambient aerosol [Rogge *et al.*, 1996; Schauer *et al.*, 1996; Fine *et al.*, 2004], making it a potentially important marker compound. Williams *et al.* [2010b] recently observed that out of a wide range of oxygenated molecular marker compounds, phthalic acid had the highest correlation with total SOA in an urban setting. Phthalic acid was strongly correlated to OA indicating the importance of the contribution of SOA to the total OA, which is consistent with the predominance of OOA. Higher phthalic acid concentrations were also associated with high mixing ratios of acetonitrile implying that biomass burning was likely an important source of SOA precursors during some periods. Interestingly, there is a clear absence of primary anthropogenic or biomass burning species (e.g., polyaromatic hydrocarbons and straight chain alkanes) in the aerosol phase and this factor is dominated by secondary compounds that are strongly correlated to OOA. TAG is sensitive to these primary non-polar compounds [Kreisberg *et al.*, 2009] so their absence suggests that they have been photochemically aged to levels below the instrumental detection limit.

Factor 2: Oxidation products of temperature-driven local biogenic emissions

The second factor included oxidation products of temperature-driven local biogenic emissions and accounted for ~35 % of the variance. Compounds loading onto this factor were a combination of monoterpene oxidation products (pinonaldehyde and nopinone), a monoterpene (*p*-cymene) and several other oxygenated terpenoids. This factor showed a very clear diurnal variation with maxima in the early hours of the morning and was slightly offset from the maximum in temperature driven monoterpene emissions [Bouvier-Brown *et al.*, 2009a] suggesting either nighttime oxidation in the canopy or transport of oxidized aged biogenic emissions during nighttime down slope flow. Observations of elevated pinonaldehyde concentrations at night were consistent with earlier measurements at the site in 2005 based on analysis of filters [Cahill *et al.*, 2006]. The magnitude of the diurnal profile was much larger during the later cold period indicating the importance of this source during the later part of the campaign.

Factor 3: Local light-driven emissions and oxidation products

The third factor included local light-driven emissions and oxidation products and accounted for ~4 % of the variance. Methyl chavicol and its oxidation product 4-methoxy benzaldehyde [Bouvier-Brown *et al.*, 2009b] loaded onto this factor. This factor was well correlated with both gas-phase methyl chavicol and 2-methyl-3-buten-2-ol (MBO) and showed a diurnal profile with a sharp early morning maximum characteristic of light driven emissions into a shallow boundary layer. This behavior was observed to be of similar intensity between both meteorological periods indicating that the contribution from this source was fairly consistent throughout the measurement period.

3.6 Observation of high vapor pressure products in the particle phase

Previous laboratory work [Tobias *et al.*, 2000] has shown that GC/MS measurements of particulate organic species can be affected by thermal decomposition artifacts for thermally labile species. However, this does not limit their value as tracers of sources provided their thermal decomposition is reproducible with time. At Blodgett, several compounds with very high vapor pressures (e.g., pinonaldehyde) were detected in the particle phase by TAG. Previously it has been reported [Odum *et al.*, 1996; Hallquist *et al.*, 1997] that pinonaldehyde is not thought to contribute to organic aerosol as result of its high vapor pressure. Pinonaldehyde has a subcooled liquid vapor pressure of 5.1 Pa at 298K [Hallquist *et al.*, 1997], corresponding to $c^* = 2.7 \times 10^5 \mu\text{g m}^{-3}$, or about 10^4 times too volatile for appreciable partitioning to the OA phase under the conditions of our study. Previous work on the molecular speciation of SOA has similarly reported of species in the particle phase whose vapor pressures are too high to support substantial partitioning from the gas phase [Forstner *et al.*, 1997b, a; Yu *et al.*, 1998; 1999a; 1999b].

These high vapor pressure compounds were most likely not collected as such, but are decomposition products of species with lower vapor pressures, e.g., oligomers or other high-MW constituents like organosulfates. They were all identified by matching mass spectra to the library and matches were very good (> 80 %), similar to the matches obtained from authentic standards, providing confidence in their assignments. These compounds spanned a wide variety of functionalities including hydrocarbons (e.g., 1-methyl-4-(1-methylethenyl)-benzene), aldehydes (e.g., cuminic aldehyde), ketones (e.g., nopinone) and multifunctional compounds (e.g., pinonaldehyde and methyl chavicol) and

were not detected in substantial quantities during filtered ambient runs when a teflon filter was switched into the sampling line (e.g., pinonaldehyde; Figure 5). This indicated that their presence was not the result of gas-phase condensation to possible adsorption sites in the collection cell. Additionally, several of these compounds could not be detected when injecting known liquid standards even at high mass loadings (> 50 ng) suggesting that the actual compounds were indeed evaporating very quickly, and that the observed compounds were most likely evolved from the particle phase during the thermal desorption or gas-chromatographic analysis cycle.

The presence of oligomeric material in the aerosols observed at Blodgett is very likely since oligomerization has been reported in chamber studies of terpene oxidation (e.g., α -pinene ozonolysis) [Gao *et al.*, 2004; Tolocka *et al.*, 2004]. Recently, Hall and Johnston [2011] reported that oligomers accounted for about 50% of the mass in SOA from α -pinene ozonolysis. It has been suggested that oligomerization takes place through aldol condensation and/or gem diol reactions following the formation of aldehydes from terpene ozonolysis [Gao *et al.*, 2004; Tolocka *et al.*, 2004] and an ion consistent with the dimer of pinonaldehyde has been detected in ambient aerosols [Tolocka *et al.*, 2004]. Another possibility would be the hydrolysis of a carbonyl compound to give a diol product [Jang *et al.*, 2002] that has a substantially lower vapor pressure. This reaction could be reversible following dehydration during thermal desorption re-liberating the original compound into the gas phase. Higher concentrations of pinonaldehyde were detected in the particle phase following the first rain event in September when relative humidities were observed to remain consistently higher, lending support to this hypothesis.

3.7 Organosulfate and nitroxyorganosulfate measurements

In total, more than 50 individual organosulfate and nitroxyorganosulfate compounds were detected and identified in high volume filter samples from both 2007 and 2009 and 16 of these compounds were quantified. In total, these 16 compounds contributed, on average, < 1 % to the OA mass. Further work describing the full set of organosulfate compounds will be presented in a forthcoming publication [Worton *et al.*, 2011]. Here we focus on only two important components that serve as markers for chemical mechanisms that lead to the incorporation of BVOCs into the particle phase. These compounds were two isomers of a five carbon triol sulfate ester formed from the reactive uptake of the recently identified dihydroxy epoxides of isoprene (IEPOX) [Paulot *et al.*, 2009] with molecular weights (MW) of 215 [Surratt *et al.*, 2010], and three isomers of a nitrooxy sulfate ester formed from α -pinene oxidation (MW 295) [Surratt *et al.*, 2008]. The IEPOX-derived organosulfate isomers are not chromatographically resolved and are therefore reported here as a combined total. The three α -pinene-derived nitrooxy sulfate ester isomers are chromatographically resolved by liquid chromatography but are also reported as a sum because it was not possible to identify which peak corresponded to which isomer due to a lack of individual authentic standards.

Figure 7 shows an intercomparison of the IEPOX-derived organosulfate measured at both Caltech and the University of Aarhus from independent solvent extractions of different aliquots of the same filters from 2007 (cold) and 2009 (hot). The correlation between the

measurements is very good but the Caltech measurements are on average a factor of four higher. We believe this is due to a calibration difference resulting from the use of different standard compounds; an organosulfate of a dihydroxy epoxide of butadiene (BEPOX) was used at Caltech while camphor sulfonic acid was used at the University of Aarhus. It is known that the efficiency of electrospray ionization is structurally dependent [Kearle, 2000] and as such the correct choice of standard is of critical importance. Due to the structural similarity of the standards used by Caltech, we expected these calibrated values to be the most appropriate and will discuss those data only from this point forwards.

Figure 8 shows time series plots of the IEPOX-derived organosulfates and the α -pinene-derived nitrooxy organosulfates for both filter collection periods, labeled as 'hot' (top panel) and 'cold' (bottom panel). It is important to note that the y-axis scale offset is a factor of six smaller between the 'hot' and 'cold' data for the IEPOX organosulfates. In general, concentrations of the IEPOX-derived organosulfates were highest during the afternoon and some morning samples in both the 'cold' and 'hot' periods were consistent with the arrival of oxidized isoprene from the band of oak trees several hours upwind of Blodgett Forest. Concentrations were, on average, a factor of ~ 10 higher during the 'hot' period in line with larger emissions of isoprene and enhanced photochemistry. These organosulfates are understood to form from heterogeneous uptake of the dihydroxy epoxides of isoprene and have been reported to be prevalent in the troposphere especially downwind of isoprene sources [Froyd *et al.*, 2010]. The mechanism is thought to proceed by acid-catalyzed ring opening of the epoxide group followed by subsequent nucleophilic addition of inorganic sulfate with the presence of highly acidic sulfate seed aerosol being of critical importance to their formation [Surratt *et al.*, 2010]. However, as discussed previously the aerosol was not acidic at our site during the study, although acidic plumes may have played a role upwind of the site.

Concentrations of the α -pinene-derived nitrooxy organosulfates were highest at night and during some morning samples (Figure 8), which would be consistent with either mixing down from aloft, from down slope transport of processed air from the previous night or overnight production from NO_3 chemistry. There is some evidence for elevated OA in the absence of 2-propyl nitrate in the early morning (Figure 6b) that could be indicative of nighttime NO_3 chemistry followed by transport to the surface the following day. However, the diurnal variation of OA does not show any substantial nighttime maxima or increases in the early morning that would be consistent with transport to the surface following overnight production aloft. This suggests that either production from NO_3 chemistry is not a dominant process or there are more important factors controlling the incorporation of these compounds into the condensed phase. Concentrations were, on average, a factor of ~ 3 higher during the 'cold' period even though concentrations of the α -pinene precursor were lower possibly consistent with other particle phase terpene oxidation products (Figure 3). The three nitrooxy-organosulfate isomers of α -pinene are thought to form from the reactive uptake of the corresponding hydroxynitrates onto acidified sulfate seed aerosols through esterification of the hydroxyl group with sulfuric acid [Surratt *et al.*, 2008]. Laboratory chamber studies of the photooxidation (α -pinene/ $\text{H}_2\text{O}_2/\text{NO}$) and nighttime oxidation (α -pinene/ NO_3 /dark) of α -pinene in the

presence of highly acidic seed aerosol produced three nitrooxyorganosulfates with the same retention times and accurate masses (MW 295) as those reported here [Surratt *et al.*, 2008]. The precursor hydroxynitrates can be generated through either OH initiated photooxidation in the presence of NO_x or NO₃ initiated oxidation [Surratt *et al.*, 2008]. It is interesting to note that the intensity of these products was larger in the NO₃ experiments and that none of these products were observed in the absence of highly acidified sulfate seed aerosol. Again the need for highly acidic aerosols in the laboratory contrasted with the neutralized aerosol at our site.

3.8 Varying BSOA contributions to OA during BEARPEX and possible couplings to NO_x and SO_x emissions

Multiple components of BSOA were observed during BEARPEX whose contributions varied as a function of time of day; isoprene oxidation products maximized in the afternoon while many terpene oxidation products were highest at night and other light and temperature derived compounds, such as methyl chavicol and its oxidation product 4-methoxybenzaldehyde, were higher at the beginning and end of the day when light driven emissions could accumulate in a shallow boundary layer. These contributions are also observed to be dependent on meteorological conditions. Contributions of isoprene oxidation products to OA appear to be more substantial during periods of higher temperatures while terpene oxidation products seem to be more important during cooler and wetter conditions and methyl chavicol oxidation seemed to contribute roughly equally to OA during both periods. Higher amounts of two oligomer decomposition products, nopinone and pinonaldehyde, were a factor of 5 higher following the first rains of the season and while monoterpene emissions are reportedly sensitive to relative humidity their concentrations were not observed to reach the same levels as during the hot period. Therefore, it appears that the amount of these terpene oxidation products that becomes incorporated into the aerosol phase may be dependent on more factors than simply the emission rate of the precursor compounds. This could suggest differences in the available oxidants or that the precursor monomers are semi-volatile in nature with a larger percentage partitioning to the condensed phase where oligomerisation reactions could occur during cooler nighttime conditions. It is apparent that any increased partitioning of BVOC oxidation products from higher concentrations of biomass burning SOA lead to significantly less enhancement of BSOA from terpene oxidation than following the rain events.

There was evidence from the correlation of OA with 2-propyl nitrate and CO along with the ¹⁴C data for potential couplings between anthropogenic emissions of NO_x and BSOA formation. This correlation suggests a possible coupling between NO_x and SOA formation that could be related to increased oxidant (i.e., OH) formation as implied from work by Carlton *et al.* [2010]. Since 2-propyl nitrate is a minor product in the photochemical production of ozone. Observations of organosulfates from isoprene and α-pinene implied a coupling between these BVOCs, NO_x and aerosol sulfate. However, concentrations of the quantified organosulfates were small and accounted for < 1 % of the total OA mass and therefore it seems unlikely in this environment that the formation of these compounds was a substantial driving force for the coupling of anthropogenic and biogenic components. We conclude that a more implicit modeling approach is warranted

to better understand the nature and importance of these couplings but is beyond the scope of this manuscript.

4. Conclusions

The organic fraction of the aerosol was dominant (~75 %) at Blodgett Forest during BEARPEX and, in the absence of sporadic wildfire influence, was on average $\sim 3 \mu\text{g m}^{-3}$ [Farmer *et al.*, 2010]. OA was predominantly oxygenated and was mostly characterized as ‘oxygenated-like’ organic aerosol (OOA). Sulfate was the most abundant inorganic component contributing on average $\sim 0.6 \mu\text{g m}^{-3}$ (~ 15 %) to the total observed aerosol loading. OA concentrations peaked at 10 – 15 $\mu\text{g m}^{-3}$ during wildfire episodes, which were also dominated by OOA, indicating the oxidized and aged state of these plumes upon arrival to the site. OA was observed to correlate with anthropogenic tracers (alkyl nitrates and CO), consistent with previous studies, and the aerosol carbon was determined to be mostly non-fossil in origin (> 75 %). This implies that the correlation between OA and an anthropogenic tracer does not necessarily identify the source of the carbon as being anthropogenic and instead implies a coupling between the anthropogenic and biogenic components in the air mass that might be related to the source of the oxidant and/or the aerosol sulfate.

Particle-phase molecular markers were dominated by secondary compounds consistent with the predominance of OOA. A factor analysis of these particle-phase markers identified three factors attributed to the following sources: (1) aged biomass burning emissions and oxidized urban emissions, (2) oxidation products of temperature-driven local biogenic emissions and (3) local light-driven emissions and oxidation products. These were generally consistent with a previous analysis of gas-phase tracers at the same site [Lamanna and Goldstein, 1999]. There was also evidence, from offline filter analysis, for an additional contribution from isoprene oxidation products. Evidence for the likely importance of aerosol sulfate, despite the neutralized nature of the aerosol at our site, was implied from the observations of organosulfates derived from isoprene and α -pinene. Although these species were not measurable by in-situ thermal desorption aerosol gas chromatography mass spectrometry (TAG). The capability to measure these highly polar and thermally labile species at higher time resolution than is currently possible from integrated filter measurements is important for further examination of the production mechanisms and fates of these compounds in aerosols.

Multiple components were observed to contribute to BSOA, which varied both diurnally and seasonally and were not solely dependent on the availability of the precursor compound. Isoprene oxidation products were more important during higher temperatures while terpene oxidation products were more abundant during the cooler and wetter periods. Several high vapor pressure products, including known oxidation products of locally emitted BVOCs (pinonaldehyde and nopinone), were detected in the particle phase as measured by TAG. We speculate that these components were evolved from the particle phase during the thermal desorption cycle and were most likely present as dimers, diols, or oligomers when originally collected. These oligomers of terpene oxidation were substantially more abundant during the cold period following the first rains of the fall season in spite of the lower observed concentrations of the precursor

compounds. This suggests an unknown mechanism is responsible for the incorporation of these compounds into the particle phase and which may be related to the availability of water in the aerosol phase although there is no definitive evidence. Further work is needed to understand this process in order to better parameterize BSOA formation in models.

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References

- Aiken, A. C., P. F. Decarlo, J. H. Kroll, et al.: O/C and OM/OC ratios of primary, secondary, and ambient organic aerosols with high-resolution time-of-flight aerosol mass spectrometry, *Environmental Science & Technology*, 42, 4478-4485, 2008.
- Aiken, A. C., B. de Foy, C. Wiedinmyer, et al.: Mexico city aerosol analysis during MILAGRO using high resolution aerosol mass spectrometry at the urban supersite (T0) - Part 2: Analysis of the biomass burning contribution and the non-fossil carbon fraction, *Atmos. Chem. Phys.*, 10, 5315-5341, 2010.
- Allan, J. D., A. E. Delia, H. Coe, et al.: A generalised method for the extraction of chemically resolved mass spectra from aerodyne aerosol mass spectrometer data, *Journal of Aerosol Science*, 35, 909-922, 2004.
- Andreae, M. O., and P. Merlet: Emission of trace gases and aerosols from biomass burning, *Glob. Biogeochem. Cycle*, 15, 955-966, 2001.
- Bahreini, R., B. Ervens, A. M. Middlebrook, et al.: Organic aerosol formation in urban and industrial plumes near Houston and Dallas, Texas, *J. Geophys. Res.-Atmos.*, 114, 2009.
- Bench, G., and P. Herckes: Measurement of contemporary and fossil carbon contents of PM_{2.5} aerosols: Results from Turtleback Dome, Yosemite National Park, *Environmental Science & Technology*, 38, 2424-2427, 2004.

893 Bench, G., S. Fallon, B. Schichtel, et al.: Relative contributions of fossil and
 894 contemporary carbon sources to PM_{2.5} aerosols at nine Interagency Monitoring for
 895 Protection of Visual Environments (IMPROVE) network sites, *J. Geophys. Res.-Atmos.*,
 896 112, 2007.

897 Bouvier-Brown, N. C., R. Holzinger, K. Palitzsch, et al.: Quantifying sesquiterpene and
 898 oxygenated terpene emissions from live vegetation using solid-phase microextraction
 899 fibers, *Journal of Chromatography A*, 1161, 113-120, 2007.

900 Bouvier-Brown, N. C., A. H. Goldstein, J. B. Gilman, et al.: In-situ ambient
 901 quantification of monoterpenes, sesquiterpenes, and related oxygenated compounds
 902 during BEARPEX 2007: implications for gas- and particle-phase chemistry, *Atmos.*
 903 *Chem. Phys.*, 9, 5505-5518, 2009a.

904 Bouvier-Brown, N. C., A. H. Goldstein, D. R. Worton, et al.: Methyl chavicol:
 905 characterization of its biogenic emission rate, abundance and oxidation products in the
 906 atmosphere, *Atmos. Chem. Phys.*, 9, 2061-2074, 2009b.

907 Brown, S. S., J. A. Degouw, C. Warneke, et al.: Nocturnal isoprene oxidation over the
 908 Northeast United States in summer and its impact on reactive nitrogen partitioning and
 909 secondary organic aerosol, *Atmos. Chem. Phys.*, 9, 3027-3042, 2009.

910 Cahill, T. M., V. Y. Seaman, M. J. Charles, et al.: Secondary organic aerosols formed
 911 from oxidation of biogenic volatile organic compounds in the Sierra Nevada Mountains
 912 of California, *J. Geophys. Res.-Atmos.*, 111, 2006.

913 Carlton, A. G., R. W. Pinder, P. V. Bhawe, et al.: To What Extent Can Biogenic SOA be
 914 Controlled?, *Environmental Science & Technology*, 44, 3376-3380, 2010.

915 Chan, A. W. H., M. N. Chan, J. D. Surratt, et al.: Role of aldehyde chemistry and NO_x
 916 concentrations in secondary organic aerosol formation, *Atmos. Chem. Phys.*, 10, 7169-
 917 7188, 2010.

918 Chan, M. N., J. D. Surratt, A. W. H. Chan, et al.: Influence of aerosol acidity on the
 919 chemical composition of secondary organic aerosol from β -caryophyllene, *Atmos. Chem.*
 920 *Phys.*, 11, 1735-1751, 2011.

921 Chen, Q., D. K. Farmer, J. Schneider, et al.: Mass spectral characterization of submicron
 922 biogenic organic particles in the Amazon Basin, *Geophysical Research Letters*, 36, 2009.

923 Cubison, M. J., A. M. Ortega, P. L. Hayes, et al.: Effects of Aging on Organic Aerosol
 924 from Open Biomass Burning Smoke in Aircraft and Laboratory Studies. , *Atmospheric*
 925 *Chemistry and Physics Discussions*, in press, 2011.

926 Day, D. A., D. K. Farmer, A. H. Goldstein, et al.: Observations of NO_x, Σ PNs, Σ ANs,
 927 and HNO₃ at a Rural Site in the California Sierra Nevada Mountains: summertime
 928 diurnal cycles, *Atmos. Chem. Phys.*, 9, 4879-4896, 2009.

929 de Gouw, J., and C. Warneke: Measurements of volatile organic compounds in the earth's
 930 atmosphere using proton-transfer-reaction mass spectrometry, *Mass Spectrometry*
 931 *Reviews*, 26, 223-257, 2007.

932 de Gouw, J. A., A. M. Middlebrook, C. Warneke, et al.: Budget of organic carbon in a
 933 polluted atmosphere: Results from the New England Air Quality Study in 2002, *J.*
 934 *Geophys. Res.-Atmos.*, 110, 2005.

935 de Gouw, J. A., A. M. Middlebrook, C. Warneke, et al.: Organic aerosol formation
 936 downwind from the Deepwater Horizon oil spill, *Science*, 331, 1295-1299, 2011.

937 DeCarlo, P. F., J. R. Kimmel, A. Trimborn, et al.: Field-deployable, high-resolution,
 938 time-of-flight aerosol mass spectrometer, *Anal. Chem.*, 78, 8281-8289, 2006.

939 DeCarlo, P. F., I. M. Ulbrich, J. Crounse, et al.: Investigation of the sources and
 940 processing of organic aerosol over the Central Mexican Plateau from aircraft
 941 measurements during MILAGRO, *Atmos. Chem. Phys.*, 10, 5257-5280, 2010.
 942 Docherty, K. S., E. A. Stone, I. M. Ulbrich, et al.: Apportionment of Primary and
 943 Secondary Organic Aerosols in Southern California during the 2005 Study of Organic
 944 Aerosols in Riverside (SOAR-1), *Environmental Science & Technology*, 42, 7655-7662,
 945 2008.
 946 Dreyfus, G. B., G. W. Schade, and A. H. Goldstein: Observational constraints on the
 947 contribution of isoprene oxidation to ozone production on the western slope of the Sierra
 948 Nevada, California, *J. Geophys. Res.-Atmos.*, 107, 2002.
 949 Duncan, B. N., J. A. Logan, I. Bey, et al.: Global budget of CO, 1988-1997: Source
 950 estimates and validation with a global model, *J. Geophys. Res.-Atmos.*, 112, 2007.
 951 Dzepina, K., R. M. Volkamer, S. Madronich, et al.: Evaluation of recently-proposed
 952 secondary organic aerosol models for a case study in Mexico City, *Atmos. Chem. Phys.*,
 953 9, 5681-5709, 2009.
 954 Ervens, B., A. G. Carlton, B. J. Turpin, et al.: Secondary organic aerosol yields from
 955 cloud-processing of isoprene oxidation products, *Geophysical Research Letters*, 35, 2008.
 956 Farmer, D. K., A. Matsunaga, K. S. Docherty, et al.: Response of an aerosol mass
 957 spectrometer to organonitrates and organosulfates and implications for atmospheric
 958 chemistry, *Proceedings of the National Academy of Sciences of the United States of*
 959 *America*, 107, 6670-6675, 2010.
 960 Farmer, D. K., J. R. Kimmel, G. Phillips, et al.: Eddy covariance measurements with
 961 high-resolution time-of-flight aerosol mass spectrometry: a new approach to chemically-
 962 resolved aerosol fluxes, *Atmospheric Measurement Techniques Discussion*, 3, 5867-
 963 5905, 2011.
 964 Fine, P. M., B. Chakrabarti, M. Krudysz, et al.: Diurnal variations of individual organic
 965 compound constituents of ultrafine and accumulation mode particulate matter in the Los
 966 Angeles basin, *Environmental Science & Technology*, 38, 1296-1304, 2004.
 967 Forstner, H. J. L., R. C. Flagan, and J. H. Seinfeld: Molecular speciation of secondary
 968 organic aerosol from photooxidation of the higher alkenes: 1-octene and 1-decene,
 969 *Atmospheric Environment*, 31, 1953-1964, 1997a.
 970 Forstner, H. J. L., R. C. Flagan, and J. H. Seinfeld: Secondary organic aerosol from the
 971 photooxidation of aromatic hydrocarbons: Molecular composition, *Environmental*
 972 *Science & Technology*, 31, 1345-1358, 1997b.
 973 Froyd, K. D., S. M. Murphy, D. M. Murphy, et al.: Contribution of isoprene-derived
 974 organosulfates to free tropospheric aerosol mass, *Proceedings of the National Academy*
 975 *of Sciences of the United States of America*, 107, 21360-21365, 2010.
 976 Gao, S., N. L. Ng, M. Keywood, et al.: Particle phase acidity and oligomer formation in
 977 secondary organic aerosol, *Environmental Science & Technology*, 38, 6582-6589, 2004.
 978 Gentner, D. R., R. A. Harley, A. M. Miller, et al.: Diurnal and seasonal variability of
 979 gasoline related volatile organic compound emissions in Riverside, California,
 980 *Environment Science and Technology*, 43, 4247-4252, 2009.
 981 Goldan, P. D., W. C. Kuster, E. Williams, et al.: Nonmethane hydrocarbon and oxy
 982 hydrocarbon measurements during the 2002 New England Air Quality Study, *J. Geophys.*
 983 *Res.-Atmos.*, 109, 2004.

984 Goldstein, A. H., N. E. Hultman, J. M. Fracheboud, et al.: Effects of climate variability
 985 on the carbon dioxide, water, and sensible heat fluxes above a ponderosa pine plantation
 986 in the Sierra Nevada (CA), *Agric. For. Meteorol.*, 101, 113-129, 2000.
 987 Goldstein, A. H., and I. E. Galbally: Known and unexplored organic constituents in the
 988 earth's atmosphere, *Environmental Science & Technology*, 41, 1514-1521, 2007.
 989 Goldstein, A. H., C. D. Koven, C. L. Heald, et al.: Biogenic carbon and anthropogenic
 990 pollutants combine to form a cooling haze over the southeastern United States,
 991 *Proceedings of the National Academy of Sciences of the United States of America*, 106,
 992 8835-8840, 2009.
 993 Grieshop, A. P., J. M. Logue, N. M. Donahue, et al.: Laboratory investigation of
 994 photochemical oxidation of organic aerosol from wood fires 1: measurement and
 995 simulation of organic aerosol evolution, *Atmos. Chem. Phys.*, 9, 1263-1277, 2009.
 996 Griffin, R. J., D. R. Cocker, R. C. Flagan, et al.: Organic aerosol formation from the
 997 oxidation of biogenic hydrocarbons, *J. Geophys. Res.-Atmos.*, 104, 3555-3567, 1999.
 998 Griffin, R. J., J. J. Chen, K. Carmody, et al.: Contribution of gas phase oxidation of
 999 volatile organic compounds to atmospheric carbon monoxide levels in two areas of the
 1000 United States, *Journal of Geophysical Research*, 112, 2007.
 1001 Guenther, A., C. N. Hewitt, D. Erickson, et al.: A global model of natural volatile organic
 1002 compound emissions, *J. Geophys. Res.-Atmos.*, 100, 8873-8892, 1995.
 1003 Guenther, A. B., P. R. Zimmerman, P. C. Harley, et al.: Isoprene and monoterpene
 1004 emission rate variability - Model evaluations and sensitivity analyses, *J. Geophys. Res.-*
 1005 *Atmos.*, 98, 12609-12617, 1993.
 1006 Hall, W. A., and M. V. Johnston: Oligomer Content of alpha-Pinene Secondary Organic
 1007 Aerosol, *Aerosol Sci. Technol.*, 45, 37-45, 2011.
 1008 Hallquist, M., I. Wangberg, and E. Ljungstrom: Atmospheric fate of carbonyl oxidation
 1009 products originating from alpha-pinene and Delta(3)-carene: Determination of rate of
 1010 reaction with OH and NO3 radicals, UV absorption cross sections, and vapor pressures,
 1011 *Environmental Science & Technology*, 31, 3166-3172, 1997.
 1012 Heald, C. L., D. J. Jacob, R. J. Park, et al.: A large organic aerosol source in the free
 1013 troposphere missing from current models, *Geophysical Research Letters*, 32, 2005.
 1014 Heald, C. L., D. A. Ridley, S. M. Kreidenweis, et al.: Satellite observations cap the
 1015 atmospheric organic aerosol budget, *Geophysical Research Letters*, 37, 5, 2010.
 1016 Hildemann, L. M., D. B. Klinedinst, G. A. Klouda, et al.: Sources of urban contemporary
 1017 carbon aerosol, *Environmental Science & Technology*, 28, 1565-1576, 1994.
 1018 Hodzic, A., J. L. Jimenez, S. Madronich, et al.: Modeling organic aerosols in a megacity:
 1019 potential contribution of semi-volatile and intermediate volatility primary organic
 1020 compounds to secondary organic aerosol formation, *Atmos. Chem. Phys.*, 10, 5491-5514,
 1021 2010a.
 1022 Hodzic, A., J. L. Jimenez, A. S. H. Prevot, et al.: Can 3-D models explain the observed
 1023 fractions of fossil and non-fossil carbon in and near Mexico City?, *Atmos. Chem. Phys.*,
 1024 10, 10997-11016, 2010b.
 1025 Holzinger, R., A. Lee, K. T. Paw, et al.: Observations of oxidation products above a
 1026 forest imply biogenic emissions of very reactive compounds, *Atmos. Chem. Phys.*, 5, 67-
 1027 75, 2005.
 1028 Hoyle, C. R., M. Boy, N. M. Donahue, et al.: A review of the anthropogenic influence on
 1029 biogenic secondary organic aerosol, *Atmos. Chem. Phys.*, 11, 321-343, 2011.

1030 Hudman, R. C., L. T. Murray, D. J. Jacob, et al.: Biogenic versus anthropogenic sources
 1031 of CO in the United States, *Geophysical Research Letters*, 35, 5, 2008.
 1032 Jang, M. S., N. M. Czoschke, S. Lee, et al.: Heterogeneous atmospheric aerosol
 1033 production by acid-catalyzed particle-phase reactions, *Science*, 298, 814-817, 2002.
 1034 Jayne, J. T., D. C. Leard, X. F. Zhang, et al.: Development of an aerosol mass
 1035 spectrometer for size and composition analysis of submicron particles, *Aerosol Sci.*
 1036 *Technol.*, 33, 49-70, 2000.
 1037 Jenkins, B. M., A. D. Jones, S. Q. Turn, et al.: Emission factors for polycyclic aromatic
 1038 hydrocarbons from biomass burning, *Environmental Science & Technology*, 30, 2462-
 1039 2469, 1996.
 1040 Jimenez, J. L., J. T. Jayne, Q. Shi, et al.: Ambient aerosol sampling using the Aerodyne
 1041 Aerosol Mass Spectrometer, *J. Geophys. Res.-Atmos.*, 108, 2003.
 1042 Jimenez, J. L., M. R. Canagaratna, N. M. Donahue, et al.: Evolution of Organic Aerosols
 1043 in the Atmosphere, *Science*, 326, 1525-1529, 2009.
 1044 Kanakidou, M., J. H. Seinfeld, S. N. Pandis, et al.: Organic aerosol and global climate
 1045 modelling: a review, *Atmos. Chem. Phys.*, 5, 1053-1123, 2005.
 1046 Kautzman, K. E., J. D. Surratt, M. N. Chan, et al.: Chemical composition of gas and
 1047 aerosol phase products from the photooxidation of naphthalene, *Journal of Physical*
 1048 *Chemistry A*, 114, 913-934, 2010.
 1049 Kebarle, P.: A brief overview of the present status of the mechanisms involved in
 1050 electrospray mass spectrometry, *Journal of Mass Spectrometry*, 35, 804-817, 2000.
 1051 Kleindienst, T. E., M. Lewandowski, J. H. Offenberg, et al.: Contribution of Primary and
 1052 Secondary Sources to Organic Aerosol and PM_{2.5} at SEARCH Network Sites, *Journal of*
 1053 *the Air & Waste Management Association*, 60, 1388-1399, 2010.
 1054 Kreisberg, N. M., S. V. Hering, B. J. Williams, et al.: Quantification of Hourly Speciated
 1055 Organic Compounds in Atmospheric Aerosols, Measured by an In-Situ Thermal
 1056 Desorption Aerosol Gas Chromatograph (TAG), *Aerosol Sci. Technol.*, 43, 38-52, 2009.
 1057 Kristensen, K., and M. Glasius: Organosulfates and oxidation products from biogenic
 1058 hydrocarbons in fine aerosols from a forest in North West Europe during spring,
 1059 Submitted to *Atmospheric Environment*, 2011.
 1060 Kroll, J. H., N. L. Ng, S. M. Murphy, et al.: Chamber studies of secondary organic
 1061 aerosol growth by reactive uptake of simple carbonyl compounds, *J. Geophys. Res.-*
 1062 *Atmos.*, 110, 2005.
 1063 Kurpius, M. R., and A. H. Goldstein: Gas-phase chemistry dominates O₃ loss to a forest,
 1064 implying a source of aerosols and hydroxyl radicals to the atmosphere, *Geophysical*
 1065 *Research Letters*, 30, 2003.
 1066 Lamanna, M. S., and A. H. Goldstein: In situ measurements of C₂-C₁₀ volatile organic
 1067 compounds above a Sierra Nevada ponderosa pine plantation, *J. Geophys. Res.-Atmos.*,
 1068 104, 21247-21262, 1999.
 1069 Levin, I., T. Naegler, B. Kromer, et al.: Observations and modelling of the global
 1070 distribution and long-term trend of atmospheric ¹⁴CO(2), *Tellus Ser. B-Chem. Phys.*
 1071 *Meteorol.*, 62, 26-46, 2010.
 1072 Lunden, M. M., D. R. Black, M. McKay, et al.: Characteristics of fine particle growth
 1073 events observed above a forested ecosystem in the Sierra Nevada Mountains of
 1074 California, *Aerosol Sci. Technol.*, 40, 373-388, 2006.

1075 M. J. Cubison, A. M. Ortega, P. L. Hayes, et al.: Effects of Aging on Organic Aerosol
 1076 from Open Biomass Burning Smoke in Aircraft and Laboratory Studies. , Atmospheric
 1077 Chemistry and Physics Discussions, in press, 2011.
 1078 Ma, Y. L., and M. D. Hays: Thermal extraction-two-dimensional gas chromatography-
 1079 mass spectrometry with heart-cutting for nitrogen heterocyclics in biomass burning
 1080 aerosols, *Journal of Chromatography A*, 1200, 228-234, 2008.
 1081 Middleton, P. (1995), Chapter 4: Sources of air pollutants, in *Composition, chemistry and*
 1082 *climate of the atmosphere*, edited by H. B. Singh, pp. 88-119, Van Nostrand Reinhold,
 1083 New York.
 1084 Murphy, J. G., A. Day, P. A. Cleary, et al.: Observations of the diurnal and seasonal
 1085 trends in nitrogen oxides in the western Sierra Nevada, *Atmos. Chem. Phys.*, 6, 5321-
 1086 5338, 2006.
 1087 Odum, J. R., T. Hoffmann, F. Bowman, et al.: Gas/particle partitioning and secondary
 1088 organic aerosol yields, *Environmental Science & Technology*, 30, 2580-2585, 1996.
 1089 Offenberg, J. H., M. Lewandowski, M. Jaoui, et al.: Contributions of biogenic and
 1090 anthropogenic hydrocarbons to secondary organic aerosol during 2006 in research
 1091 Triangle Park, NC, *Aerosol and Air Quality Research*, 11, 99-108, 2011.
 1092 Paulot, F., J. D. Crounse, H. G. Kjaergaard, et al.: Unexpected Epoxide Formation in the
 1093 Gas-Phase Photooxidation of Isoprene, *Science*, 325, 730-733, 2009.
 1094 Peltier, R. E., A. P. Sullivan, R. J. Weber, et al.: No evidence for acid-catalyzed
 1095 secondary organic aerosol formation in power plant plumes over metropolitan Atlanta,
 1096 Georgia, *Geophysical Research Letters*, 34, 2007.
 1097 Pierotti, D., S. C. Wofsy, D. Jacob, et al.: Isoprene and its oxidation products -
 1098 methacrolein and methyl vinyl ketone, *J. Geophys. Res.-Atmos.*, 95, 1871-1881, 1990.
 1099 Pye, H. O. T., and J. H. Seinfeld: A global perspective on aerosol from low-volatility
 1100 organic compounds, *Atmos. Chem. Phys.*, 10, 4377-4401, 2010.
 1101 Rhead, M. M., and R. D. Pemberton: Sources of naphthalene in diesel exhaust emissions,
 1102 *Energy Fuels*, 10, 837-843, 1996.
 1103 Robinson, A. L., N. M. Donahue, M. K. Shrivastava, et al.: Rethinking organic aerosols:
 1104 Semivolatile emissions and photochemical aging, *Science*, 315, 1259-1262, 2007.
 1105 Rogge, W. F., L. M. Hildemann, M. A. Mazurek, et al.: Mathematical modeling of
 1106 atmospheric fine particle-associated primary organic compound concentrations, *J.*
 1107 *Geophys. Res.-Atmos.*, 101, 19379-19394, 1996.
 1108 Schade, G. W., A. H. Goldstein, and M. S. Lamanna: Are monoterpene emissions
 1109 influenced by humidity?, *Geophysical Research Letters*, 26, 2187-2190, 1999.
 1110 Schade, G. W., and A. H. Goldstein: Fluxes of oxygenated volatile organic compounds
 1111 from a ponderosa pine plantation, *J. Geophys. Res.-Atmos.*, 106, 3111-3123, 2001.
 1112 Schauer, J. J., W. F. Rogge, L. M. Hildemann, et al.: Source apportionment of airborne
 1113 particulate matter using organic compounds as tracers, *Atmospheric Environment*, 30,
 1114 3837-3855, 1996.
 1115 Schichtel, B. A., W. C. Malm, G. Bench, et al.: Fossil and contemporary fine particulate
 1116 carbon fractions at 12 rural and urban sites in the United States, *J. Geophys. Res.-Atmos.*,
 1117 113, 2008.
 1118 Seinfeld, J. H., and J. F. Pankow: Organic atmospheric particulate material, *Annual*
 1119 *Review of Physical Chemistry*, 54, 121-140, 2003.

1120 Simoneit, B. R. T., J. J. Schauer, C. G. Nolte, et al.: Levoglucosan, a tracer for cellulose
 1121 in biomass burning and atmospheric particles, *Atmospheric Environment*, 33, 173-182,
 1122 1999.
 1123 Slowik, J. G., C. Stroud, J. W. Bottenheim, et al.: Characterization of a large biogenic
 1124 secondary organic aerosol event from eastern Canadian forests, *Atmos. Chem. Phys.*, 10,
 1125 2825-2845, 2010.
 1126 Spracklen, D. V., J. L. Jimenez, K. S. Carslaw, et al.: Aerosol mass spectrometer
 1127 constraint on the global secondary organic aerosol budget, *Atmospheric Chemistry and*
 1128 *Physics Discussions*, 11, 5699-5755, 2011.
 1129 Stuiver, M., and H. A. Polach: Reporting of C14 Data - Discussion, *Radiocarbon*, 19,
 1130 355-363, 1977.
 1131 Sullivan, A. P., R. E. Peltier, C. A. Brock, et al.: Airborne measurements of carbonaceous
 1132 aerosol soluble in water over northeastern United States: Method development and an
 1133 investigation into water-soluble organic carbon sources, *J. Geophys. Res.-Atmos.*, 111,
 1134 2006.
 1135 Surratt, J. D., S. M. Murphy, J. H. Kroll, et al.: Chemical composition of secondary
 1136 organic aerosol formed from the photooxidation of isoprene, *Journal of Physical*
 1137 *Chemistry A*, 110, 9665-9690, 2006.
 1138 Surratt, J. D., J. H. Kroll, T. E. Kleindienst, et al.: Evidence for organosulfates in
 1139 secondary organic aerosol, *Environmental Science & Technology*, 41, 517-527, 2007.
 1140 Surratt, J. D., Y. Gomez-Gonzalez, A. W. H. Chan, et al.: Organosulfate formation in
 1141 biogenic secondary organic aerosol, *Journal of Physical Chemistry A*, 112, 8345-8378,
 1142 2008.
 1143 Surratt, J. D., A. W. H. Chan, N. C. Eddingsaas, et al.: Reactive intermediates revealed in
 1144 secondary organic aerosol formation from isoprene, *Proceedings of the National*
 1145 *Academy of Sciences of the United States of America*, 107, 6640-6645, 2010.
 1146 Szidat, S., T. M. Jenk, H. W. Gäggeler, et al.: Radiocarbon (14C)-deduced biogenic and
 1147 anthropogenic contributions to organic carbon (OC) of urban aerosols from Zürich,
 1148 Switzerland, *Atmospheric Environment*, 38, 4035-4044, 2004.
 1149 Takahama, S., C. I. Davidson, and S. N. Pandis: Semicontinuous measurements of
 1150 organic carbon and acidity during the Pittsburgh air quality study: Implications for acid-
 1151 catalyzed organic aerosol formation, *Environmental Science & Technology*, 40, 2191-
 1152 2199, 2006.
 1153 Tobias, H. J., K. S. Docherty, D. E. Beving, et al.: Effect of relative humidity on the
 1154 chemical composition of secondary organic aerosol formed from reactions of 1-
 1155 tetradecene and O₃, *Environmental Science & Technology*, 34, 2116-2125, 2000.
 1156 Tolocka, M. P., M. Jang, J. M. Ginter, et al.: Formation of oligomers in secondary
 1157 organic aerosol, *Environmental Science & Technology*, 38, 1428-1434, 2004.
 1158 Tsimpidi, A. P., V. A. Karydis, M. Zavala, et al.: Evaluation of the volatility basis-set
 1159 approach for the simulation of organic aerosol formation in the Mexico City metropolitan
 1160 area, *Atmos. Chem. Phys.*, 10, 525-546, 2010.
 1161 Tunved, P., H. C. Hansson, V. M. Kerminen, et al.: High natural aerosol loading over
 1162 boreal forests, *Science*, 312, 261-263, 2006.
 1163 Volkamer, R., J. L. Jimenez, F. San Martini, et al.: Secondary organic aerosol formation
 1164 from anthropogenic air pollution: Rapid and higher than expected, *Geophysical Research*
 1165 *Letters*, 33, 2006.

1166 Volkamer, R., F. S. Martini, L. T. Molina, et al.: A missing sink for gas-phase glyoxal in
 1167 Mexico City: Formation of secondary organic aerosol, *Geophysical Research Letters*, 34,
 1168 2007.
 1169 Wang, L., R. Atkinson, and J. Arey: Dicarbonyl products of the OH radical-initiated
 1170 reactions of naphthalene and the C-1- and C-2-alkylnaphthalenes, *Environmental Science*
 1171 *& Technology*, 41, 2803-2810, 2007.
 1172 Weber, R. J., A. P. Sullivan, R. E. Peltier, et al.: A study of secondary organic aerosol
 1173 formation in the anthropogenic-influenced southeastern United States, *J. Geophys. Res.-*
 1174 *Atmos.*, 112, 2007.
 1175 Williams, B. J., A. H. Goldstein, N. M. Kreisberg, et al.: An in-situ instrument for
 1176 speciated organic composition of atmospheric aerosols: Thermal Desorption Aerosol
 1177 GC/MS-FID (TAG), *Aerosol Sci. Technol.*, 40, 627-638, 2006.
 1178 Williams, B. J., A. H. Goldstein, D. B. Millet, et al.: Chemical speciation of organic
 1179 aerosol during the International Consortium for Atmospheric Research on Transport and
 1180 Transformation 2004: Results from in situ measurements, *J. Geophys. Res.-Atmos.*, 112,
 1181 2007.
 1182 Williams, B. J., A. H. Goldstein, N. M. Kreisberg, et al.: In situ measurements of
 1183 gas/particle-phase transitions for atmospheric semivolatile organic compounds,
 1184 *Proceedings of the National Academy of Sciences of the United States of America*, 107,
 1185 6676-6681, 2010a.
 1186 Williams, B. J., A. H. Goldstein, N. M. Kreisberg, et al.: Major components of
 1187 atmospheric organic aerosol in southern California as determined by hourly
 1188 measurements of source marker compounds, *Atmos. Chem. Phys.*, 10, 11577-11603,
 1189 2010b.
 1190 Worton, D. R., A. H. Goldstein, J. D. Surratt, et al.: Measurements of organosulfates,
 1191 nitroxy-organosulfates and acids observed during the biosphere effects on aerosol and
 1192 photochemistry experiment. , Manuscript in preparation for *Atmospheric Chemistry and*
 1193 *Physics*, 2011.
 1194 Yu, J. Z., R. C. Flagan, and J. H. Seinfeld: Identification of products containing -COOH,
 1195 -OH, and -C=O in atmospheric oxidation of hydrocarbons, *Environmental Science &*
 1196 *Technology*, 32, 2357-2370, 1998.
 1197 Yu, J. Z., D. R. Cocker, R. J. Griffin, et al.: Gas-phase ozone oxidation of monoterpenes:
 1198 Gaseous and particulate products, *J. Atmos. Chem.*, 34, 207-258, 1999a.
 1199 Yu, J. Z., R. J. Griffin, D. R. Cocker, et al.: Observation of gaseous and particulate
 1200 products of monoterpene oxidation in forest atmospheres, *Geophysical Research Letters*,
 1201 26, 1145-1148, 1999b.
 1202 Zhang, Q., D. R. Worsnop, M. R. Canagaratna, et al.: Hydrocarbon-like and oxygenated
 1203 organic aerosols in Pittsburgh: insights into sources and processes of organic aerosols,
 1204 *Atmos. Chem. Phys.*, 5, 3289-3311, 2005.
 1205 Zhang, Q., J. L. Jimenez, M. R. Canagaratna, et al.: Ubiquity and dominance of
 1206 oxygenated species in organic aerosols in anthropogenically-influenced Northern
 1207 Hemisphere midlatitudes, *Geophysical Research Letters*, 34, 2007a.
 1208 Zhang, Q., J. L. Jimenez, D. R. Worsnop, et al.: A case study of urban particle acidity and
 1209 its influence on secondary organic aerosol, *Environmental Science & Technology*, 41,
 1210 3213-3219, 2007b.
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Table 1. Total carbon mass analysed (mg C), aerosol loading (PM_{2.5}; µg C m⁻³) and fraction of modern carbon determined from the radiogenic (¹⁴C) carbon results. For comparison the aerosol loading (PM₁; µg C m⁻³) from the AMS averaged onto the same timescale as the filter samples are also shown.

Sampling Period (MM/DD hh:mm)	Sample Volume (m ³) ^a	Mass Analysed (µg C) ^a	Aerosol Loading (µg C m ⁻³) ^b		Fraction Modern ^b
			filter	AMS ^c	
field blank	0	210 ± 40	-	-	< 0.06
09/21 13:05 – 09/21 18:30	32.2	300 ± 10	2.77 ± 1.63	0.90 ± 0.06	1.21 ± 0.39
09/21 18:45 – 09/22 07:15	74.2	430 ± 10	2.87 ± 0.71	1.08 ± 0.11	1.00 ± 0.13
09/25 18:45 – 09/26 07:15	74.2	470 ± 10	3.46 ± 0.71	0.92 ± 0.09	0.81 ± 0.09
09/26 07:30 – 09/26 16:00	50.3	390 ± 10	3.44 ± 1.04	0.82 ± 0.10	0.89 ± 0.14
09/26 19:00 – 09/27 07:15	73.2	530 ± 10	4.33 ± 0.72	1.10 ± 0.09	0.76 ± 0.07
09/27 07:30 – 09/27 12:50	32.0	330 ± 10	3.66 ± 1.64	0.54 ± 0.05	0.69 ± 0.16
09/27 13:05 – 09/27 17:15	24.7	310 ± 10	3.80 ± 2.12	0.93 ± 0.14	0.67 ± 0.19
09/27 17:30 – 09/28 07:15	81.6	560 ± 10	4.23 ± 0.64	1.10 ± 0.25	0.69 ± 0.06

^a Volume and mass correspond to 36 cm² aliquots of each filter (total area 412 cm²).

^b The aerosol loading and fraction modern data have been blank corrected.

^c Conversion of µg m⁻³ to µg C m⁻³ assuming a OM/OC ratio of 1.9 for OOA aerosol [Aiken *et al.*, 2008].

1220 **Table 2.** Compounds identified by thermal desorption aerosol gas chromatography
 1221 (TAG) along with the results of a factor analysis approach.
 1222

Compound Name (molecular formula)	CAS registry number	Uncertainty of compound identification	Loadings (values < 0.4 omitted)		
			F1	F2	F3
1-methyl-4-(1-methylethenyl)- benzene (C ₁₀ H ₁₂)	1195-32-0	medium		0.98	
Levoglucosenone (C ₆ H ₆ O ₃)	37112-31-5	low	0.74		
benzoic acid, 2-hydroxy methyl ester (C ₈ H ₈ O ₃)	119-36-8	medium	0.67	0.48	
p-methyl acetophenone (C ₉ H ₁₀ O)	122-00-9	medium		0.86	
4,7-dimethylbenzofuran (C ₁₀ H ₁₀ O)	28715-26-6	low		0.88	
cuminic aldehyde (C ₁₀ H ₁₂ O)	122-03-2	medium		0.79	
1-cyclohexene-1- carboxaldehyde (C ₁₀ H ₁₄ O)	1192-88-7	medium		0.71	
1-(3H)-isobenzofuranone (C ₈ H ₆ O ₂)	87-41-2	low	0.92		
methyl chavicol (C ₁₀ H ₁₂ O)	140-67-0	medium			0.56
triacetin (C ₉ H ₁₄ O ₆)	102-76-1	medium	0.85		
benzoic acid (C ₇ H ₆ O ₂)	65-85-0	low	0.97		
phthalic acid (C ₈ H ₆ O ₄)	88-99-3	low	0.95		
4-methoxybenzaldehyde (C ₈ H ₈ O ₂)	123-11-5	medium			0.67
1H-indene-1,3(2H)-dione (C ₉ H ₆ O ₂)	606-23-5	low	0.89		
1H-isoindole-1,3(2H)-dione (C ₈ H ₅ NO ₂)	85-41-6	low	0.87		
3-methyl phthalic acid (C ₉ H ₆ O ₃)	37102-74-2	low	0.97		
4-methyl phthalic acid (C ₉ H ₆ O ₃)	4316-23-8	low	0.84		
Nopinone (C ₉ H ₁₄ O)	24903-95-5	medium		0.89	
Pinonaldehyde (C ₁₀ H ₁₆ O ₂)	2704-78-1	medium		0.91	
p-cymene (C ₁₀ H ₁₄)	99-87-6	medium		0.96	
unknown m/z 119 (RT 23 mins)	-	high		0.89	
Importance of Factors					
Sum square loadings			8.04	7.24	0.94
Proportion of variance			0.38	0.35	0.04
Cumulative variance			0.38	0.73	0.77

1223 Factor analysis was performed in SPLUS 6.2 (MathSoft Inc.), using varimax rotation and principal factors
1224 extraction. The model was limited to three factors because additional factors had very low sum square
1225 loadings and did not explain any substantial portion of the variance. Proportion variance defines the
1226 fraction of the data explained by each factor. Uncertainty of compound identification is divided into three
1227 categories (i.e., low, medium and high); high uncertainty for compounds which could not be identified from
1228 mass spectral library matches or from known standards, medium uncertainty for compounds with better
1229 matches and low uncertainty for compounds with very good library matches , which were also retention
1230 time matched to authentic standards.
1231

Figure Captions

Figure 1. (a) Bulk aerosol composition (organics, sulfate, nitrate, ammonium and chloride) as measured by the aerosol mass spectrometer (AMS), indicating the prevalence of the carbonaceous fraction. (b) Organic aerosol divided into ‘hydrocarbon like’ (HOA) and ‘oxygenated like’ (OOA) shown along with acetonitrile, a gas phase tracer for biomass burning.

Figure 2. (a) Scatter plot of organic aerosol (OA) versus 2-propyl nitrate for BEARPEX (this work; black circles) and the New England air quality study (NEAQS [*de Gouw et al.*, 2005]; grey squares). The radiogenic carbon (^{14}C) data is shown as filled white squares and the BEARPEX data is color coded by acetonitrile to show that the ^{14}C sampling period was not influenced by biomass burning. (b) Scatter plot of OA vs 2-propyl nitrate filtered by acetonitrile (<0.2 ppb) and separated into three time periods; early morning (07:00 – 09:00; orange circles), midday (12:00 – 14:00; red circles) and early evening (19:00 – 21:00; blue circles).

Figure 3. Comparison of the diurnal variation of organic aerosol (OA), sum of methyl vinyl ketone and methacrolein (MVK + MACR), α -pinene and isopentane, separated into the two meteorological periods; hot (top panel) and cold (bottom panel).

Figure 4. Time series plots of the sum of methyl vinyl ketone and methacrolein (MVK+MACR) and particle phase biogenic oxidation tracers pinonaldehyde and nopinone as measured by TAG showing their varying behavior during the hot and cold periods and following the first rains in early fall.

Figure 5. Temporal and diurnal variations of the four major particle phase tracer compounds (1 - phthalic acid and levoglucosenone; 2 - pinonaldehyde; 3 - methyl chavicol) that represent the three major sources (1 - oxidized urban emissions and aged biomass burning emissions; 2 - oxidation of a temperature driven local biogenic emissions; 3 - local light driven biogenic emissions and their oxidation products) identified from a factor analysis that impacted the site during both the identified meteorological periods.

Figure 6. Time series plot of the fraction of pinonaldehyde in the gas and particle phases, according to TAG measurements, for the entire campaign showing that the observation of pinonaldehyde was not the result of a gas phase collection artifact. The diurnal variation of pinonaldehyde for the entire campaign (inset) showing the predominance of higher abundances at night.

Figure 7. Intercomparison of the IEPOX organosulfates measured at the University of Aarhus and Caltech.

Figure 8. Time series of the most dominant biogenic organosulfate compounds, IEPOX organosulfates (solid black lines), methacrolein (MACR) organosulfate (dashed black

1277 lines) and α -pinene nitroxy-organosulfates (dotted gray lines), observed during a 5 day
1278 period of high volume filter collections. Shaded bars indicate nighttime.
1279

Supplementary Information

Figure S1. (a) Regression of OOA versus acetonitrile separated into the hot and cold periods. This plot illustrates the good correlation during the hot period and this slope was used to estimate the likely biomass burning contribution (BBOA) to OA from the acetonitrile measurements. The lack of correlation during the cold period (inset) indicates that biomass burning was likely not an important source of OA in the cold period. (b) Comparison of the estimated BBOA to measured OA during only the hot period. The error bars reflect the uncertainty in these values based on the error in the slope from Figure S1a used to derive their values.

Figure S2. Comparison of organic carbon ($\mu\text{g C m}^{-3}$) measured by the AMS and the high volume filters. X-axis error bars represent the standard deviation in the averaged AMS data and y-axis error bars are the total uncertainty in the filter organic carbon measurements.

Figure S3. Correlation of CO (open circles) to organic aerosol (OA) during both meteorological periods at BEARPEX. The OA data was filtered for acetonitrile > 0.175 ppb to remove the influence of biomass burning sources of OA. The CO data was filtered by windspeeds > 1 m/s to remove generator spikes that influenced the site under stagnant conditions. The OA data has been converted to $\mu\text{g sm}^{-3}$ to be consistent with previous studies [DeCarlo *et al.*, 2010; Cubison *et al.*, 2011].